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Amphiphilic Poly(*N*-isopropylacrylamides) Prepared by Using a Lipophilic Radical Initiator: Synthesis and Solution Properties in Water

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ABSTRACT: Amphiphilic poly(*N*-isopropylacrylamides) (PNIPAM) substituted with two pendant *n*-octadecyl groups at the chain end were prepared by free-radical polymerization in dioxane of *N*-isopropylacrylamide (NIPAM) using 4,4′-azobis(4-cyano-*N*,*N*-dioctadecyl)pentanamide (DODA-501) as the initiator. Copolymers differing in the molar ratio of octadecyl groups to *N*-isopropylacrylamide units were obtained by varying the initiator to monomer ratio. Their composition was established by ^{1}H NMR spectroscopy. The solution properties of the polymers were studied as a function of polymer concentration and temperature. Quasi-elastic light scattering measurements and fluorescence experiments with two probes, pyrene and bis(1-pyrenylmethyl) ether (dipyme), reveal the existence of multimolecular micelles below the lower critical solution temperature (LCST) in solutions of concentration exceeding ca. 0.1 g L^{-1}. The micelles consist of a rigid core of octadecyl chains and a corona of solvated PNIPAM chains. These collapse at the LCST. The collapsed micelles aggregate, resulting in macroscopic phase separation of the solutions.

Introduction

Water-soluble polymers containing a few hydrophobic substituents per chain exhibit unusual properties. Even in dilute solutions they may act as powerful rheology modifiers in fluids often referred to as "associative thickeners".[1] The rheological properties of these fluids depend very much on the type of hydrophobic group attached to the polymer backbone and on the number of alkyl groups per chain. Whether the alkyl groups are added at random along the polymer chain or appended at one or at both ends of the chain also affects significantly the properties of the fluids.[2,3] We reported recently the synthesis and solution properties of amphiphilic derivatives of poly(*N*-isopropylacrylamide) (PNIPAM), consisting of a PNIPAM backbone carrying a small number of long alkyl chains.[4] The polymers differed in the length of the alkyl chain, C_{10}, C_{14}, C_{18}, and in the number of *n*-alkyl groups per *N*-isopropylacrylamide units (molar ratios: 1/100 and 1/200). Schild and Tirrell also described amphiphilic PNIPAM derivatives in which the hydrophobic groups were hexadecyl groups incorporated at the 1 mol % level.[5] In all cases the alkyl groups were attached at random to the macromolecules which were prepared by free-radical copolymerization of *N*-isopropylacrylamide (NIPAM) and a given *N*-*n*-alkylacrylamide.

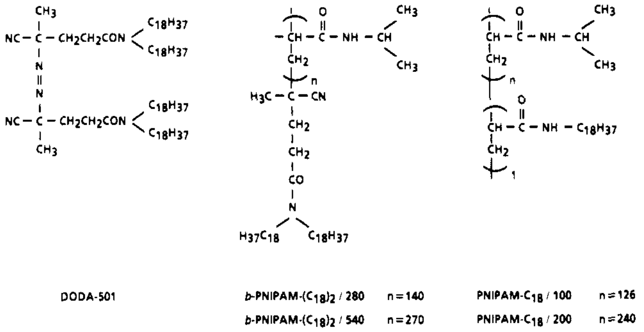

Figure 1. Chemical structures of the amphiphilic initiator and polymers described in this study.

We describe here the synthesis and solution properties of two members of another type of amphiphilic poly(*N*-isopropylacrylamide), which consists of a PNIPAM chain substituted at one end with a hydrophobic group. The polymers were prepared by free-radical polymerization of NIPAM using a lipophilic initiator, 4,4′-azobis(4-cyano-*N*,*N*-dioctadecyl)pentanamide (DODA-501; Figure 1). Chemical composition and molecular weight parameters of the copolymers were determined by ^{1}H NMR, GPC, and viscosity measurements. A preliminary investigation of the solution properties in water of these copolymers was conducted using quasi-elastic light scattering (QELS) measurements and fluorescence probe experiments. Evidence is given for the formation of polymeric micelles in aqueous solutions below and above their lower critical solution temperature. A comparison with amphiphilic PNIPAM's randomly substituted with octadecyl groups highlights the crucial role of the molecular architecture of the macromolecules in determining their properties in water.

Experimental Section

Materials. Water was purified with a Millipore Milli-Q System. Dioxane was purified by distillation from sodium under nitrogen. *N*-Isopropylacrylamide (NIPAM; Eastman Kodak Chemicals) was purified by recrystallization from toluene/hexane (10/1, v/v). The lipophilic initiator DODA-501 was prepared by reaction of dioctadecylamine with disuccinimidyl 4,4′-azobis(4-cyanovalerate) as described previously.[6] Pyrene (99%; Aldrich Chemicals Co.) was purified by repeated recrystallizations from ethanol and subsequent sublimation. Dipyme was a gift from Professor M. A. Winnik, University of Toronto.[7] The polymers PNIPAM-C_{18}/100 and PNIPAM-C_{18}/200 were prepared and purified as described previously.[4]

Polymerizations. *b*-PNIPAM-$(C_{18})_2$/280 (NIPAM/DODA-501, 100/1): NIPAM (2.7 mmol, 307 mg) and DODA-501 (0.027

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Table I
Physical Properties of the Polymers

polymer	NIPAM-C$_{18}$^{a}	DP^a	M_n^{a}	[η], mL g^{-1}	M_v^{b}	M_n^{c}	M_w^{c}	M_w/M_n	ref
PNIPAM				39.0	190 000	39 000	137 000	4.55	
b-PNIPAM-(C$_{18}$)$_2$/280	140:1	280	32 000	21.5	140 000	25 000	78 000	3.14	
b-PNIPAM-(C$_{18}$)$_2$/540	270:1	540	61 000	17.8	110 000	20 000	74 000	3.33	
PNIPAM-C$_{18}$/200	240:1			39.7	370 000	17 000	27 000	1.64	4
PNIPAM-C$_{18}$/100	126:1			39.7	370 000	23 000	38 000	1.66	4

[a] Determined by NMR (see text). [b] From $[\eta] = 9.59 \times 10^{-3} M_v^{0.65}$ (Fujishige, S. *Polym. J.* 1987, *19*, 297). [c] By GPC (relative to polystyrene).

mmol, 35 mg) were dissolved in dioxane (5 mL). The solution was degassed by bubbling with N$_2$ for 10 min. It was heated to 70 °C for 17 h. The polymer was recovered by precipitation in hexane (50 mL). It was dissolved in THF (1 mL) and reprecipitated in ether (250 mL). The polymer was separated by filtration and dried in vacuo at 40 °C for 24 h (218 mg, 67%).

***b*-PNIPAM-(C$_{18}$)$_2$/540 (NIPAM/DODA-501, 200/1)**: This polymer was prepared by the same procedure, starting with NIPAM (5.51 mmol, 618 mg) and DODA-501 (0.030 mmol, 39 mg) and yielding 590 mg of purified polymer (93%).

PNIPAM: NIPAM (0.127 mol, 14.29 g) and AIBN (0.72 mmol, 119 mg) were dissolved in dioxane (240 mL). The solution was degassed by bubbling with N$_2$ for 10 min. It was heated to 60 °C for 3.5 h. The polymer was recovered by precipitation in hexane (2.0 L). It was dissolved in THF (25 mL) and reprecipitated in ether (2 L). The polymer was separated by filtration and dried in vacuo at 40 °C for 24 h (12.74 g, 89%).

Instrumentation. Proton NMR spectra were recorded for CDCl$_3$ solutions of the polymers at ambient temperature on a Bruker AMX400 spectrometer operating at a ^{1}H frequency of 400.14 MHz. UV absorption spectra were recorded with a Hewlett Packard 8480A diode array spectrometer. Temperature-controlled experiments were done with a Hewlett-Packard 89100A temperature control accessory consisting of a digitally controlled thermoelectrically heating and cooling cell holder with cell stirring capability and programmed temperature ramping (heating or cooling rate: 0.2 °C min^{-1}). The temperature of the sample fluid was measured with a Hewlett-Packard 89102A Teflon-coated temperature-sensitive probe. Gel permeation chromatography was performed with a Waters system equipped with a Waters 410 refractive index detector. Four Ultrastyragel columns (10 000, 5,000, 500, and 100 Å) were used. The eluent (THF) was used at a flow rate of 1.0 mL min^{-1}. Solution viscosities were measured at 27 °C with a Viskotek Model 100 differential viscometer. The polymers were dissolved in THF at concentrations of ca. 80 ppm. Cloud points were determined by spectrophotometric detection of changes in turbidity of solutions heated at a constant rate in a magnetically stirred UV-cell, as described previously.[8] Micelle sizes were determined by quasi-elastic light scattering (QELS) with a fixed 90° scattering angle, using a Brookhaven Instrument Corp. particle sizer Model BI-90 equipped with a He/Ne laser.

Fluorescence Measurements. Fluorescence spectra were recorded on a SPEX Fluorolog 212 spectrometer equipped with a DM3000F data system. The temperature of the water-jacketed cell holder was controlled with a Neslab circulating bath. The temperature of the sample fluid was measured with a thermocouple immersed in the sample. Solutions were not degassed. Excitation spectra were measured in the ratio mode. Emission spectra were not corrected. They were recorded with an excitation wavelength of 336 nm (pyrene) or 348 nm (dipyme). Excitation slitwidths were set at 3.6 nm, and emission slitwidths were set at 0.9 nm. Solutions for analysis with pyrene were prepared by dilution of stock solutions of the polymers and pyrene with water saturated with pyrene (ca. 6 × 10^{-7} mol L^{-1}). Samples containing dipyme (ca. 1 × 10^{-7} mol L^{-1}) were prepared by adding a concentrated solution of dipyme (3–5 μL, 1.3 × 10^{-4} mol L^{-1} in acetone) to aqueous solutions of the polymers (5 mL, 3 g L^{-1}). The solutions were sonicated for 10 min in an ultrasonic bath (Cole-Parmer). They were kept at room temperature in the dark until equilibrated (2 days).[9]

Results and Discussion

Synthesis and Characterization of the Copolymers. The synthesis of end-alkylated PNIPAM was accomplished in dioxane, a solvent for both the monomer, *N*-isopropylacrylamide, and the initiator, DODA-501. On the basis of our previous experience with amphiphilic PNIPAM's, we were confident that the end-alkylated PNIPAM's would be soluble in dioxane. This was indeed the case for two polymers obtained starting with monomer/initiator ratios of 200/1 and 100/1. Several precipitations with THF/diethyl ether were performed to purify the polymers. An AIBN-initiated polymerization of NIPAM was performed under identical conditions, yielding a control sample. Polymers with reasonably high molecular weights and broad molecular weight distributions were obtained in all cases, as seen by GPC analysis and intrinsic viscosity values of THF solutions (Table I). The average numbers of monomer units per *n*-octadecyl groups were determined from an analysis of the ^{1}H NMR spectra of CDCl$_3$ solutions. The ratio of isopropyl to C$_{18}$ groups was calculated from the area of the singlet at 3.97 ppm due to the resonance of the isopropylidene proton of the monomer unit and the area of the triplet centered at 0.85 ppm, attributed to the terminal methyl protons of the octadecyl chain. Numbers of NIPAM units per dioctadecylamino groups of 280 and 540 were calculated for polymers prepared with initial monomer/initiator ratios of 100/1 and 200/1, respectively. Consistent with our previous nomenclature, we designate these polymers as *b*-PNIPAM-(C$_{18}$)$_2$/280 and *b*-PNIPAM-(C$_{18}$)$_2$/540, respectively.[10]

The number of monomer units per polymer end group calculated by NMR should correspond to the degree of polymerization of the polymers, assuming that termination occurred by disproportionation and not chain coupling.[11] The situation, however, is more complicated. The first indication is that the apparent M_n is larger than the initiator to monomer feed ratio by a factor of approximately 2, indicating that the polymerization yield, based on the initiator, is 50% or less. This value is in fact in agreement with the yields reported previously by Kitano et al. for DODA-501-initiated polymerizations of acrylic acid.[6] Further complexities are apparent in Table I. From the GPC results one can obtain a reasonable estimate of the breadth of the molecular weight distribution (M_w/M_n). But M_w values determined in THF do not correspond to the M_w values inferred from M_w/M_n and M_n obtained from NMR data. A number of reasons may account for these ambiguities. They concern the details of the termination process, especially the role of chain-transfer processes. Also, possible association of the end groups in THF may affect the viscosity measurements. Such issues will become increasingly important as one tries to get a detailed understanding of the phenomena. For the purpose of this paper interested in the global description of end-group micellization in water these uncertainties in MW can be neglected.

Finally, from the data presented here it is not possible to ascertain unambiguously that some polymers do not carry dioctadecyl groups at both ends. The assumption that substitution occurred at only one end of each macromolecule is (1) based on the mechanism of free-

Table II
Properties of the Polymers in Water

polymer	LCST, °C	$\bar{d}$,[a] nm	polydispersity[b]	$[I_1/I_3]^{DP}$ 20 °C	$[I_1/I_3]^{DP}$ 35 °C	I_E/I_M 20 °C	I_E/I_M 35 °C	ref
b-PNIPAM-$(C_{18})_2$/280	31.5	73 ± 6	0.16 ± 0.01	1.12	1.18	0.20	0.17	
b-PNIPAM-$(C_{18})_2$/540	32.0	72 ± 5	0.12 ± 0.02	1.13	1.19	0.20	0.15	
PNIPAM-C_{18}/200	30.3	38 ± 1	0.21 ± 0.01	1.23	1.30	0.13	0.06	9
PNIPAM-C_{18}/100	25.6	42 ± 1	0.23 ± 0.01	1.20	1.22	0.10	0.07	9

[a] Effective diameter, measured at 20 °C. [b] Polydispersity = μ_2/Γ, where Γ and μ_2 are the first two moments of the measured distribution ($\mu_2 = (D^2 - \bar{D}^2)q^4$ and $\Gamma = \bar{D}q^2$ (q = scattering vector).

radical polymerization with termination taking place by disproportionation or chain transfer and (2) by analogy with results obtained during the DODA-initiated polymerization of acrylic acid.[12] In this case it was shown that polymers prepared in the presence of a chain-transfer agent, hence substituted at one end only, had the same properties as those prepared without additional chain-transfer agent. Work is in progress to clarify these points.

Properties of the Copolymers in Water. Evidence for Micelle Formation. Both end-alkylated polymers were soluble in water at or below room temperature. As expected the aqueous solutions became turbid when heated, signaling the occurrence of a lower critical solution temperature (LCST). This temperature for each polymer is very close to that of PNIPAM (32 °C)[13] (Table II). This seems surprising, since as a rule the LCST of a polymer in water decreases with increasing hydrophobicity.[14] This unusual effect suggests that the alkyl chains are not exposed to water but rather form a micellar structure protected from the water by the PNIPAM chains, and therefore they do not make a hydrophobic contribution to the LCST. A similar effect was observed in the case of amphiphilic PNIPAM's carrying at random a small number of octadecyl chains.[4] That such micellar structures form was confirmed by quasi-elastic light scattering measurements and fluorescence probe experiments described next.

Simple quasi-elastic light scattering experiments performed at a fixed angle (Brookhaven particle sizer) gave no signal with PNIPAM solutions (3 g L^{-1}) in agreement with previous reports of the absence of interchain aggregation in PNIPAM solutions below their LCST.[15] By contrast similar QELS experiments on the end-alkylated copolymers in water (3 g L^{-1}) showed a very strong signal, indicating the presence of micelles. Their sizes are reported as effective diameters, $\bar{d}$, determined by a cumulant analysis of the data (Table II). From the calculated polydispersity values it is apparent that there is a broad distribution of micelle sizes. The sizes were insensitive to changes in temperature below the LCST, but extensive aggregation above this temperature prevented any reliable measurements from being performed. The randomly substituted copolymers, PNIPAM-C_{18}/100 and PNIPAM-C_{18}/200, also form micelles in water, with a broad size distribution but smaller effective diameter than the end-alkylated copolymers (Table II).

It is worth noting that there is a difference in micelle size below the LCST for the two types of amphiphilic PNIPAM's. Despite the fact that their molecular weights (M_w) are smaller, the end-alkylated polymers form larger micelles than the randomly-alkylated micelles. This difference may reflect either that PNIPAM-C_{18} forms predominantly unimolecular micelles or that the aggregation number is much smaller than that for the block copolymers. The micelle size is dictated primarily by the action of two competing forces: (1) the hydrophobic forces[16] on the alkyl groups in water which sequester them at the aggregate center and (2) the excluded-volume repulsion between the polymers which limits the aggregate size. It is expected that the balance of these two forces will be quite different for the two types of copolymers.

Characterizing the Hydrophobic Clusters. In polymers of this sort it is expected that hydrophobic groups associate to form localized structures, hydrophobic in nature with properties related to those of surfactant micelles. A common way to test for the presence of such structures is to examine the fluorescence spectra of dyes whose emission gives indications on changes in the polarity and rigidity of the environment. Fluorescence experiments were performed with two hydrophobic probes, pyrene and bis(1-pyrenylmethyl) ether (dipyme). First, pyrene (ca. 8 × 10^{-7} mol L^{-1}) was added to solutions of the copolymers in water. Changes in the fine structure of the pyrene emission were monitored as a function of polymer concentration. Specifically, the ratio $[I_1/I_3]^{Py}$ of the intensity of the (0,0) band (I_1) to that of the band at 386 nm (I_3) was measured. This ratio is used routinely in the study of micellar structures in water.[17] It takes a high value in polar media (1.81 for pyrene in water). It decreases with increasing polarity (1.12 for pyrene solubilized in sodium dodecyl sulfate micelles). In aqueous solutions of PNIPAM below the LCST the ratio takes a value close to that of pyrene in water (ca. 1.80) even at high polymer concentrations.

By contrast, in the case of the end-alkylated PNIPAM's the ratio decreased rapidly with increasing polymer concentration to reach a constant value of ca. 1.20 for polymer concentrations higher than 0.5 g L^{-1}. This value is much lower than that of PNIPAM solutions, indicating the presence of hydrophobic microdomains capable of solubilizing the hydrophobic pyrene probe. From a plot of $[I_1/I_3]^{Py}$ as a function of polymer concentration (Figure 2a), it is possible to estimate the concentration corresponding to the onset of aggregation. The data indicate that association begins at concentrations of ca. 5 × 10^{-2} and 9.1 × 10^{-2} g L^{-1} for *b*-PNIPAM-$(C_{18})_2$/280 and *b*-PNIPAM-$(C_{18})_2$/540, respectively. The association transition appears to be very broad, spanning almost a 100-fold range in polymer concentration. A similar observation has been reported by Wang and Winnik for the aggregation of poly(ethylene oxides) tagged at both ends with hexadecyl groups.[18] Another perspective on the aggregation phenomenon may be gained from a plot of the changes in $[I_1/I_3]^{Py}$ with octadecyl group concentration (Figure 2b). Surprisingly, here we observe that the micropolarity sensed by pyrene is the same in solutions of the end-alkylated copolymers and of the randomly alkylated copolymers over the entire concentration range, with the onset of micelle formation occurring at ca. 4 × 10^{-5} mol L^{-1}. This observation emphasizes the predominant role of the hydrophobic forces acting on the octadecyl chains in the micellization process.[19-21]

Dipyme is a probe not only of local polarity but also of local viscosity. It forms an intramolecular excimer. The

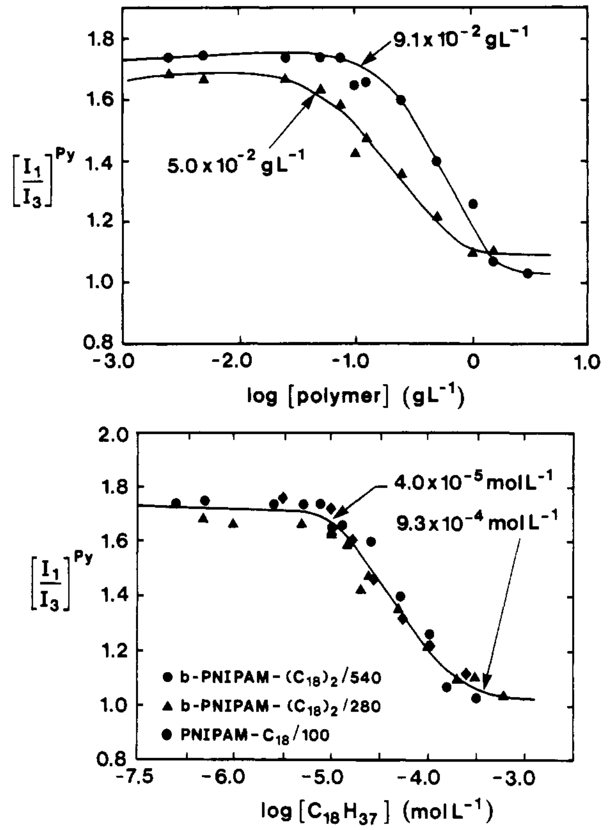

Figure 2. Plots of the changes in the ratio $[I_1/I_3]^{Py}$ for pyrene in aqueous solutions of amphiphilic poly(*N*-isopropylacrylamides) as a function of polymer concentration (logarithmic scale), expressed in g L^{-1} (top) and in octadecyl group concentration (mol L^{-1}) (bottom) (20 °C, λ_{exc} 336 nm; data for PNIPAM-C_{18}/100, see ref 4).

extent of excimer emission depends upon the rate of conformational change of the chain linking the two pyrenyl groups. The motion is resisted by the local friction imposed by the environment. As a consequence, the excimer to monomer intensity ratio, I_E/I_M, provides a measure of the fluidity of the dipyme environment. The vibrational fine structure in the dipyme monomer emission is sensitive to the polarity of the probe microenvironment. The ratio $[I_1/I_3]^{DP}$ reports on local polarity in much the same way as $[I_1/I_3]^{Py}$, but the absolute values are not the same for the two probes in identical environments. Values of $[I_1/I_3]^{DP}$ and I_E/I_M are reported in Table II for dipyme in aqueous solutions of the end- and randomly-alkylated PNIPAM's. The values of I_E/I_M point to a rigid structure for the octadecyl chain clusters formed in these solutions. Interestingly the ratios are higher than those for dipyme solubilized in the octadecyl clusters of the randomly-alkylated copolymers. This is a significant result, which points to differences in cluster morphology. The values of $[I_1/I_3]^{DP}$ support this observation: they indicate a more hydrophobic environment for dipyme in the octadecyl clusters of PNIPAM-$(C_{18})_2$ copolymers.

Temperature Effects. The temperature dependencies of the ratios $[I_1/I_3]^{Py}$, $[I_1/I_3]^{DP}$, and I_E/I_M were monitored for solutions of the copolymers (1.0 and 3.0 g L^{-1}). In each case the $[I_1/I_3]^{Py}$ ratios increased slightly and reached a limiting value, 1.22 for *b*-PNIPAM-$(C_{18})_2$/280 and 1.29 for *b*-PNIPAM-$(C_{18})_2$/540, in solutions heated above their LCST. Note that these values show only a small amount of temperature sensitivity and are on the low side of the $[I_1/I_3]^{Py}$ range (1.33 ± 0.1) reported previously for pyrene in solutions of PNIPAM and its amphiphilic derivatives above their LCST.[3] Similarly the emission of dipyme in these solutions does not show significant changes with temperature. This is in contrast with the observations reported for dipyme in solutions of PNIPAM-C_{18}/100 or PNIPAM-C_{18}/200 above their LCST (Table II). In this case the dipyme experiments bring strong evidence that the hydrophobic pockets are disrupted at the LCST. In the case of the end-alkylated PNIPAM's there is no indication that the hydrophobic clusters are destroyed, implying a much stronger association of the octadecyl groups (Figure 3).

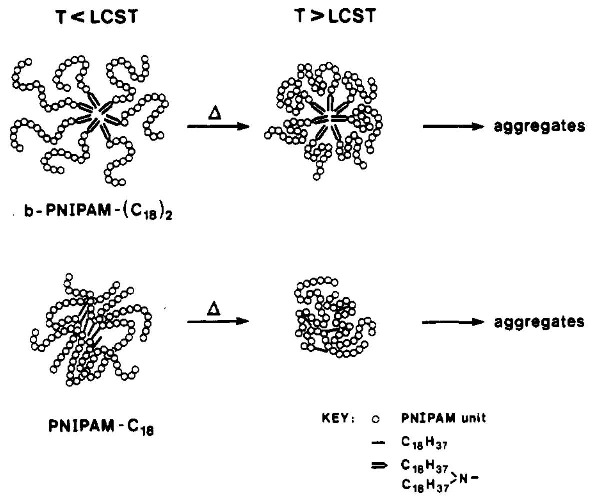

Figure 3. Schematic representation of the thermally-induced polymer conformational changes for *b*-PNIPAM-$(C_{18})_2$ and PNIPAM-C_{18}.

Conclusions

The end-alkylated poly(*N*-isopropylacrylamide) derivatives prepared with the lipophilic initiator DODA-501 form micelles in water, with a rigid core of octadecyl chains and a diffuse corona of solvated PNIPAM chains. The core is capable of solubilizing hydrophobic dyes, such as pyrene and dipyme. From changes with temperature of the emission of these fluorescent probes we conclude that at the LCST the PNIPAM chains collapse on the surface of the micellar core. Concomitant with the chain collapse, intermicellar aggregation takes place. This results in macroscopic phase separation. The original micelles, it would seem, conserve the morphology they adopted in the solutions below the LCST. Viewed at the molecular level this phase-separation process differs in several key aspects from that occurring in solutions of the randomly alkylated amphiphilic PNIPAM's. In solutions of these copolymers phase separation triggers a disruption of the hydrophobic clusters formed below the LCST and a more isotropic distribution of the octadecyl chains within the polymer-rich phase. This phase is much less polar than in the case of PNIPAM itself but substantially more polar than the interior of the clusters formed by aggregation of pendant octadecyl groups. Further work is in progress to confirm these and other differences between the two classes of amphiphilic poly(*N*-isopropylacrylamides).

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